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Assessment of Activity of 'Transparent and Clear' and 'Opaque and Highly Coloured' Photocatalytic Samples using a Fluorescent Photocatalytic Activity Indicator Ink, *FPaii*.

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Abstract

The photocatalytic activity of self-cleaning glass is assessed using a resazurin (Rz) photocatalyst activity indicator ink, i.e. Rz *paii*, via both the rate of change in the colour of the ink (blue to pink), $R(Abs)$, and the rate of change in the fluorescence intensity, $R(Fl)$, ($\lambda(\text{excitation}) = 593 \text{ nm}$; $\lambda(\text{emission}) = 639 \text{ nm}$) of the ink. In both cases the kinetics are zero order. Additional work with a range of glass samples of different photocatalytic activity reveal $R(Abs)$ is directly related to $R(Fl)$, thereby showing that the latter, like the former, can be used to provide a measure of the photocatalytic activity of the sample under test. The measured value of $R(Fl)$ is found to be the same for 5 pieces of, otherwise identical, self-cleaning glass with: black, red, blue, yellow and no coloured tape stuck to their backs, which demonstrates that $R(Fl)$ measurements can be used to measure photocatalytic activity under conditions of high colour and opacity under which $R(Abs)$ cannot be measured. The relevance of this novel, fluorescence-based *paii* to the assessment of the activity of highly coloured, opaque photocatalytic samples, such as paints and tiles, is discussed briefly.

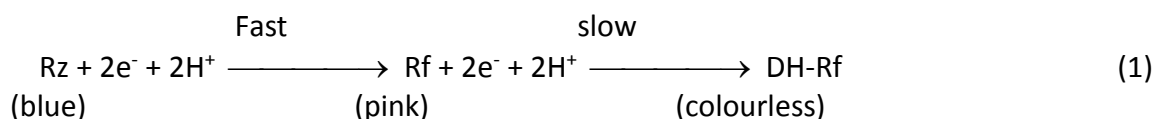
Key words: fluorescence, absorbance, photocatalyst, activity, opaque, coloured

1. Introduction

Semiconductor-sensitised photocatalysis is a well-established and growing area of research, innovation and commercialisation [1]. Most commercial examples of photocatalytic products are described as 'self-cleaning' [1,2] and include: glass, tiles, concrete, paint and fabrics [1,3,4]. In almost all such cases the active ingredient is TiO_2 , which absorbs UV light, from a solar or an artificial light source, to produce an electron-hole pair, h^+e^- , which can back-react, either in the bulk of the semiconductor, or at its surface or, most importantly with regard to photocatalysis, react with surface-adsorbed species [5]. With regard to the latter process, the photogenerated electron, e^- , can react with ambient O_2 to produce, ultimately, H_2O , whereas the photogenerated hole, h^+ , can oxidise most organic species [1]. The ability of TiO_2 to photocatalyse what is effectively the 'cold combustion' of most surface-adsorbed organics is the main photocatalytic property responsible for its ability to maintain a clean, sterile, hydrophilic surface which are the commonly promoted features of most commercial photocatalytic products [6].

In photocatalysis, it is clearly important to be able to assess and compare the activities of new and existing commercial and research semiconductor photocatalytic materials. It is not surprising to note, therefore, that, over the years, a number of different tests have been developed into ISO standards for this very purpose [7]. These tests include, for example, the photobleaching of methylene blue in aqueous solution [8] and the photo-oxidation of NO_x gases [9]. Unfortunately, these tests typically take a long time (3-5 hours) to run, use expensive analytical equipment and require a dedicated technician to operate them [7]. It follows that there is a need for a fast, simple and easily performed test of activity for, amongst other things: quality assurance, marketing and rapid screening of the new and existing photocatalytic materials.

Recent work within the group has shown that by coating the photocatalyst film with a photocatalyst activity indicator ink (*paii*), and irradiating the combination with UVA light, a striking colour change is effected, usually within minutes, (when UV irradiance = 2 mW cm^{-2}), and at a rate which provides a measure of the photocatalytic activity of the underlying photocatalyst film [10]. The basic components of a typical *paii* are: a redox dye, such as blue-coloured, Resazurin, Rz , which is readily and irreversibly reduced by the photogenerated electrons on the TiO_2 , i.e.



Where Rf is resorufin and DH-Rf is dihydro-resorufin [11,12]. Reaction (1) is very efficient because the ink also contains a vast excess of glycerol, which reacts very fast and irreversibly with the photogenerated holes [13], to yield glyceraldehyde and, eventually, glyceric acid [11,12]. Subsequent work, using a test pollutant in the form of: (i) a thin solid

organic film (stearic acid) [14,15] and (ii) an oxidisable gaseous pollutant, NO, [16], has established, for a range of photocatalysts of different activity, that there is a direct correlation between the initial rates of *paii* reduction and the rates of oxidation of these very different test pollutants. Other work shows that the kinetics of Rz reduction via reaction (1) can be monitored not only using UV/Vis spectrophotometry, but also via RGB colour analysis, using a mobile phone digital camera and appropriate colour analysis App [17]. It is perhaps no surprise then, that the Rz *paii* is in the process of being considered by ISO as a fast, simple method for assessing the photocatalytic activity of thin film materials [18].

A great deal of the work on *paiis* has used self-cleaning glass as the test material, i.e. a test material that is both colourless and transparent [11]. If the sample under test is opaque and moderately coloured (e.g. beige), such as is the case for many self-cleaning tiles and most self-cleaning paints, *paii* technology can still be employed, by using RGB colour analysis to monitor the photocatalysed reduction of the redox dye and so provide a measure of the rate of reaction (1) [16,19]. If the sample under test was highly coloured, but clear, as in coloured glass for example, then, depending upon the colour, it is might still be possible to measure the kinetics of reduction of the *paii*, via UV/Vis spectrophotometry or RGB colour analysis. Although, under the latter circumstances, any black, blue and red coloured samples would present an obvious, significant challenge to using a Rz *paii*.

From the above, it follows that, if the sample under test was both opaque and highly coloured, as can be the case for some commercial samples of photocatalytic tiles or paints, then it would seem unlikely that *paii* technology could be used to assess the photocatalytic activity. However, this apparent 'limitation' to the applicability of *paii* technology presumes that the assessment of the concentration of the redox dye in the *paii*, as a function of irradiation time, t , requires the accurate measurement of the colour of the indicator film, *via* either UV/Vis absorbance measurements (which is only appropriate for clear samples) or diffuse reflectance/RGB analysis (usually appropriate for opaque samples) [10,20]. Note that the latter techniques are only appropriate for use with opaque, but NOT highly coloured samples. However, this potential 'limitation' to *paii* technology is removed if the redox dye in the *paii*, in its oxidised (D_{ox}) and/or reduced (D_{red}) form, is fluorescent, since the concentration of one or both of the latter species could then be monitored via the variation in the intensity of fluorescence as a function of t and so allow a value for the rate of photocatalysis to be determined. Fortunately, both Rz and Rf luminesce, as indicated by some of the key photophysical features of Rz and Rf in aqueous solution [21] given in Table 1.

Thus, in this paper we report on the use of a fluorescent *paii*, i.e. an *FPaii*, to measure the photocatalytic activities of not only traditional 'transparent and clear' photocatalytic samples, but also ones that are 'opaque and highly coloured'. To our knowledge this is the first report of a fluorescence-based *paii*.

Table 1: Photophysical features of Rz and Rf in aqueous solution [21] and in a *paii*

	Rz	Rf
Aqueous solution:		
Absorption $\lambda_{\text{max}}/\text{nm}$	602	572
Fluorescence $\lambda_{\text{max}}/\text{nm}$	634	585
Quantum yield of fluorescence	0.11	0.74
<i>Paii</i> film:		
Absorption $\lambda_{\text{max}}/\text{nm}$	609	582
Fluorescence $\lambda_{\text{max}}/\text{nm}$	639	598

2. Experimental

2.1 Materials

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and obtained in the highest purity possible. We thank Saint Gobain for supplying a sample of their commercial, transparent, and clear self-cleaning glass, BioClean™.

2.2 Methods

The method used to prepare the Rz ink has been described in detail elsewhere [10]. However, briefly, 0.15 g of hydroxyethyl cellulose, HEC, (CAS No.: 9004-62-0; viscosity: 145 mPa s for 1 wt% solution in water) were dissolved into 9.85 g water to a yield a 1.5 wt% solution of the polymer, to which were then added sequentially and dissolved: 1 g of glycerol, followed by 10 mg of Rz, (CAS No.: 62758-13-8; purity 75%) and 20 mg of the surfactant, polysorbate 20 (CAS No.: 9005-64-5). The ink was then stirred with a magnetic stirrer for a minimum of 8 h and stored in a fridge when not being used.

In this work the self-cleaning glass samples under test were cut into 10 × 45 mm rectangle (so as to fit diagonally in a 1 cm fluorescence cell, *vide infra*). In accordance with the pre-cleaning procedures employed by most ISO tests for photocatalysts [7], each test sample was cleaned using a methanol-soaked, silicone-free, tissue followed by drying in air for 10 min and irradiating with UV light (to remove any organic surface impurities) for at least 15 hours.

All UV-Vis spectra and absorbance data were recorded using a Varian Cary 60 Bio UV-Visible spectrophotometer. All irradiations were carried out using 2 x 4 W UVA tubes, with a principal wavelength of 352 nm, and an irradiance of approximately 2 mW cm⁻². *Paii* films on the samples under test were made using the Rz ink, *via* a draw-down method [20], using a wire-wound bar, i.e. a K-bar, that is used regularly in the print industry to deposit ink films

of known thickness [22]. In this work a K-bar No. 3 was used to yield a wet ink film thickness of 24 μm on the surface of the sample under test, that becomes $2.0 \pm 0.1 \mu\text{m}$, when dried in air for 60 min. The latter thickness was measured using the Swanepoel interference fringe method [17]. All fluorescence measurements were made using a Perkin Elmer LS5B Fluorimeter.

2.3 Absorbance and Fluorescence Measurements

The absorbance and fluorescence spectrum of the Rz *paii* on the sample under test was monitored regularly as a function of irradiation time by removing the sample periodically from the UV light source and placing it in the UV/Vis spectrophotometer and then the fluorimeter, respectively. In making the absorbance measurements, the sample was placed always in the same position, directly in the path of the absorbance monitoring beam of the instrument. In order to achieve the same high degree of reproducibility in the making the fluorescence measurements, the sample was always placed in the diagonal of an otherwise empty 1 cm quartz fluorescence cell held firmly in the sample cell of the fluorimeter, so that the ink-coated sample was perpendicular to the excitation beam and parallel to the emission intensity monitoring system of the instrument. This arrangement was found to be particularly effective with regards reproducibility, for clear and opaque samples alike, since much of the emission from the Rz/Rf ink film emerged from the edges of the glass sample under test, presumably via a total internal reflection process. In all this work a $\lambda(\text{excitation})$ value of 593 nm was used to generate the fluorescence spectra.

3. Results and Discussion

3.1 Transparent and Clear Photocatalytic Samples

Self-cleaning glass from St. Gobain, i.e. BioCleanTM, is clear and transparent, with a thin coating of TiO_2 on its surface which is responsible for the 'self-cleaning' action of the product. When coated with the Rz ink, using a K-bar No. 3, and UV-irradiated, the blue Rz ink initially turns pink, due to Rf formation and then, eventually, colourless upon prolonged irradiation, see reaction (1). Figure 1 provides photographs of the Rz-coated clear glass sample before and after 20 min UV irradiation which illustrates the distinctive initial (blue to pink) colour change associated with a UV-irradiated *paii* on a photocatalytically-active sample. The last of these photographs is that of the 20 min UV irradiated film, recorded NOT under room light illumination (as were the other two), but under a low level of UV illumination, since the latter reveals the highly fluorescence nature of the Rf dye in the photocatalytically-reduced Rz *paii*.



Figure 1: From left to right, photographs of a Rz-coated clear BioClean™ glass sample: (i) before UV irradiation, (ii) after 20 min UV irradiation and (iii) as in (ii) but under low UV light illumination in order to reveal the highly fluorescent nature (photographed here) of the photocatalytically generated Rf.

In addition to photographing the samples, the changes in UV/Vis spectrum of the Rz ink film were recorded as a function of UV irradiation time and the results are illustrated in figure 2.

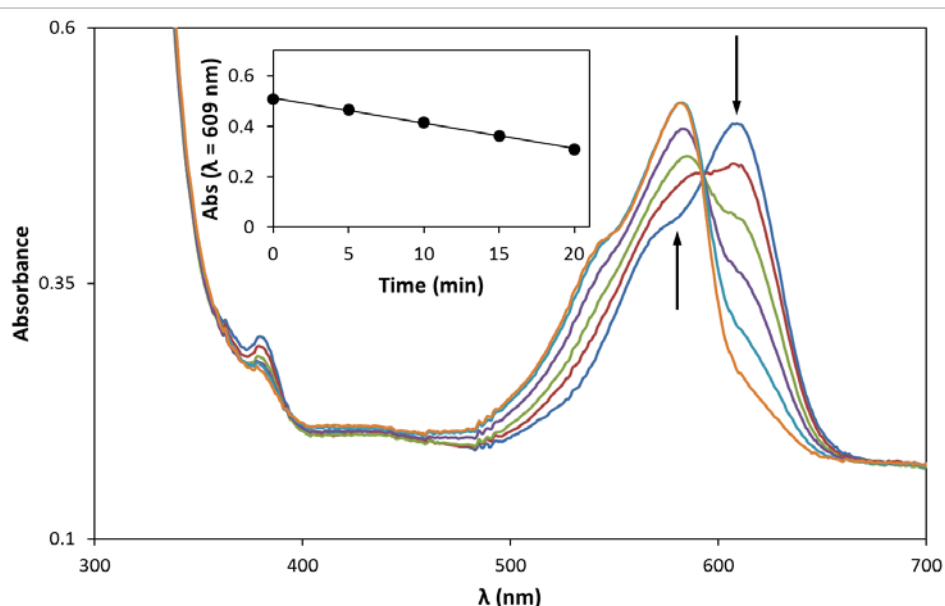


Figure 2: UV/Vis spectrum of the Rz ink film on a sample of BioClean™ recorded as a function of UV irradiation time, t , the spectra were recorded for the following times: 0, 5, 10, 15, 20 and 25 min. The arrows depict the direction of change in absorbance at 609 nm (due to the reduction of Rz) and 582 nm (due to the production of Rf) as the Rz *Paii*/photocatalytic sample is UV irradiated. The insert diagram is a plot of the absorbance at 609 nm as a function of t , using data taken from the main diagram, the gradient of which provides a value for $R(Abs)$ for the sample under test.

From these results, it is clear that the blue Rz dye ($\lambda_{\max} = 609 \text{ nm}$) is initially converted its pink reduced form, Rf, ($\lambda_{\max} = 582 \text{ nm}$), as the value of the absorbance at $\lambda_{\max} = 609 \text{ nm}$ (due to Rz) decreased, while that at $\lambda_{\max} = 582 \text{ nm}$ (due to Rf) increased, *via* reaction (1) and the well-defined isosbestic point at 593 nm, suggests no other species is involved, such as DH-Rf, during this initial phase of the photocatalysed reduction of the Rz dye; this is because the subsequent reduction of Rf (to DH-Rf) is slow as indicated in reaction (1). The insert diagram in figure 2 is a plot of the absorbance of the film at 609 nm, and therefore a

measure of the concentration of Rz in the indicator film, $[Rz]$, as a function of irradiation time, t . The latter plot illustrates the well-established zero-order nature of the decay kinetics as the Rz dye is reduced via reaction (1), accompanied by a zero-order growth in absorbance at 582 nm due to Rf formation, the gradient of either of which, $R(Abs)$, can be taken as a measure of the activity of the underlying photocatalytic film.

As indicated by the data in table 1, both Rz and Rf luminesce, and, since neither shows a big Stokes shift, there is significant degree of overlap in absorption spectra and luminescence spectra. The last photograph in Figure 1 illustrates the luminescence of an Rf film on self-cleaning glass. In this work, the fluorescent measurements were simplified by using the wavelength of the isosbestic point at 593 nm as the excitation wavelength for all emission measurements, since it yielded a fluorescent spectrum with just one peak ($\lambda_{max} = 639$ nm, see table 1), which increased with irradiation time, as the emission due to Rz was replaced with the much stronger emission (even at 639 nm) of Rf. A typical set of emission spectra, recorded as a function of irradiation time, for the same Rz film on BioClean™ glass sample as used to generate the absorbance data in figure 2, is illustrated in figure 3 below. This latter data was used to construct the insert diagram in figure 3, namely, a plot of the luminescence intensity at 639 nm (I_{639}) of the Rz film as a function of irradiation time. This plot is a straight line, with a gradient, $R(FI)$. The linear nature of this plot is as expected given the previously noted zero-order kinetics exhibited by the Rz *paii* on most materials including self-cleaning glass.

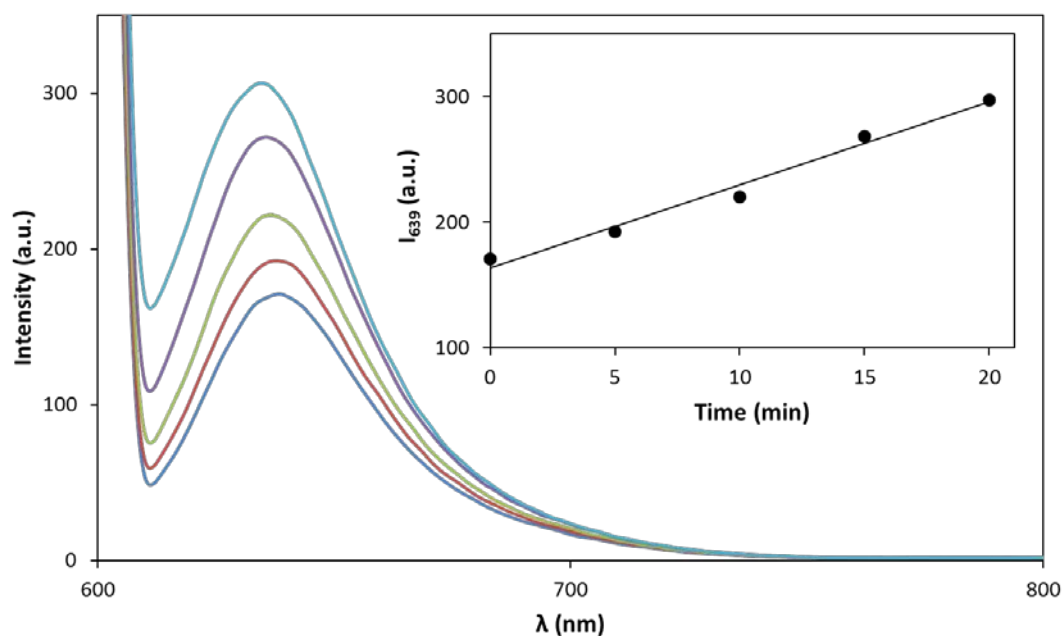


Figure 3: Fluorescence spectrum ($\lambda(\text{excitation}) = 593$ nm) of the Rz ink film on a sample of BioClean™ recorded as a function of UV irradiation time, the spectra were recorded (from bottom to top) for the following times: 0, 5, 10, 15 and 20 min, respectively. The insert diagram is a plot of the fluorescence intensity at 639 nm as a function of t , using data taken from the main diagram, the gradient of which provides a value for $R(FI)$ for the sample under test.

The results of the above work show that the absorbance and fluorescence changes for one sample of self-cleaning glass obey zero-order kinetics. However, obviously this observation does not necessarily mean that the rates, i.e. $R(Abs)$ and $R(Fl)$, will be related directly to each other when the Rz ink is used on other samples with different photocatalytic activities. The direct dependence of $R(Fl)$ on $R(Abs)$ needs to be established clearly before it can be reasonably claimed that $R(Fl)$, like $R(Abs)$, can be used to provide a measure of the activity of a photocatalytic sample under test.

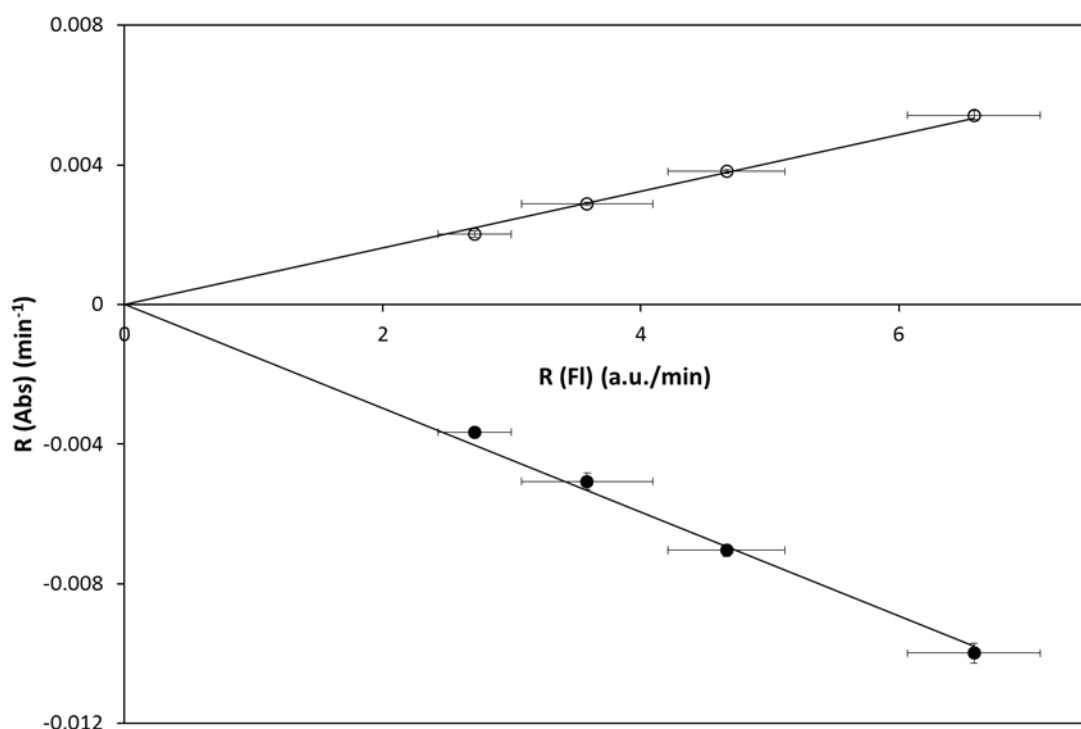


Figure 4: Measured rates of absorbance growth ($\lambda = 582$ nm) and simultaneous decay ($\lambda = 609$ nm) as a function of measured rates of fluorescence growth ($\lambda(\text{emission}) = 639$ nm) for BioClean™ samples heated at 450°C for the following times: 6, 3, 1 and 0 h.

In order to establish the above critical relationship between $R(Abs)$ and $R(Fl)$, a series of self-cleaning glass samples with different photocatalytic activities were prepared by heating them at 450°C for increasing amounts of time, since previous work had established that BioClean™ glass can be deactivated significantly with prolonged heat treatment at this temperature [19]. In this way, samples of self-cleaning glass with decreasing activity were prepared by using the following heating times: 0, 1, 3 and 6 h. Each heat-conditioned sample was then tested for photocatalytic activity using the Rz *Paii*, in which the photocatalysed reduction of the Rz to Rf was monitored spectrophotometrically both at 582 nm (for which positive values of $R(Abs)$ were recorded as Rf is generated and thus the

absorbance at 582 nm increases, see figure 2) and 609 nm (for which negative values of $R(Abs)$ were recorded as R_z is reduced and thus the absorbance at 609 nm increases, see figure 2). In addition, at the same time the latter absorbance measurements were made, the increase in the fluorescence of the R_z *paii* was also monitored ($\lambda(\text{excitation}) = 593$ nm; $\lambda(\text{emission}) = 639$ nm) to yield a positive value of $R(Fl)$ for each sample. The results of this work are illustrated in figure 4, the top part of which is a plot of $R(Abs)$ at 582 nm vs $R(Fl)$ for the different samples tested and the bottom part is a plot of $R(Abs)$ at 5609 nm vs $R(Fl)$ for the same samples. These two plots show that $R(Abs)$, based on *either* the growth in the absorbance due to R_f generation *or* the decrease in absorbance due to R_z loss) and $R(Fl)$, are indeed correlated directly, there-by suggesting that $R(Fl)$, like $R(Abs)$, can be used to provide a measure of the activity of photocatalytic materials such as self-cleaning glass.

3.2 Opaque and Highly Coloured Photocatalytic Samples

In order to demonstrate that fluorescence measurements can be used to assess the photocatalytic activity of opaque and highly coloured samples, 4 out of 5 identical samples of self-cleaning glass had their non-photocatalyst coated backs covered with black, red, blue and yellow plastic tape, so as to render the samples both opaque and highly coloured. Photographs of these samples: (i) before, (ii) after coating with R_z ink, and (iii) after UV irradiation are illustrated in figure 5.

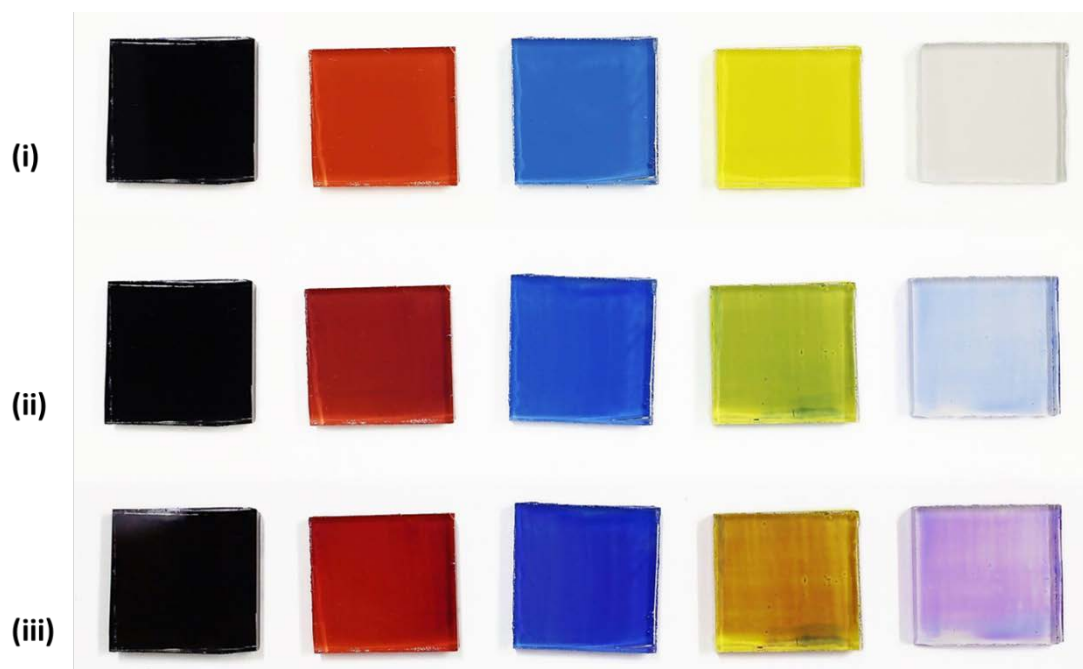


Figure 5: photographs of 5 identical pieces of self-cleaning glass (from top to bottom): (i) with no R_z ink coating, (ii) with an R_z ink coating and (iii) as in (ii) but after UV irradiation for 20 min.

From the results of this work it is clear that only the yellow and colourless samples of glass would allow the rate of R_z to R_f conversion to be monitored easily *via* the colour change

associated with the photocatalysed reaction (1), using diffuse reflectance/RGB analysis, say. This simple experiment highlights the major limitation of the current absorbance-based *paii* technology for measuring photocatalytic activity, namely, that the samples under test cannot be highly coloured, especially if the colours have a high blue, black or red content.

However, encouragingly, all five highly coloured samples exhibited a measurable degree of luminescence that could be monitored as a function of irradiation time, as the R_z ink was converted to R_f to yield individual values for $R(FI)$ for each sample. The results of this work, a plot of $R(FI)$ versus colour of sample for the 5 samples illustrated in figure 5, are illustrated in figure 6 and show that the rate of fluorescence growth at 639 nm was independent of sample background colour, as would be expected for five identical samples of self-cleaning glass, whatever their colour or opacity.

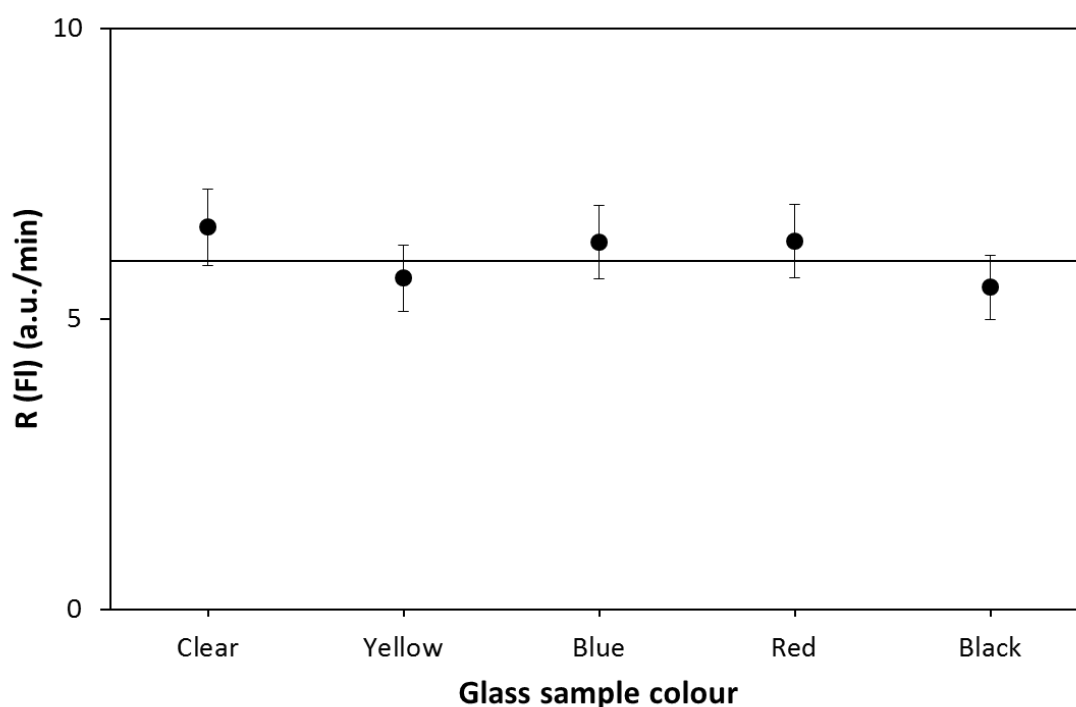


Figure 6: Measured rates of fluorescence intensity growth ($\lambda(\text{excitation}) = 593 \text{ nm}$; $\lambda(\text{emission}) = 639 \text{ nm}$) for the same R_z ink on self-cleaning glass with different coloured background colours, as illustrated in figure 5.

4. Conclusions

Photocatalytic activity can be assessed using a photocatalyst activity indicator ink, such as the R_z ink, either *via* the rate of change in the colour of the ink (blue to pink), or, if the sample is highly coloured, via the rate of change in the fluorescence intensity of the ink, since the latter is directly related to the former, which, in turn, have been directly related to more traditional tests of photocatalytic activity, such as the oxidation of stearic acid [14,15]

or NO [16]. These results will prove of great interest to all those working in the field of photocatalysis, especially those researchers and industries that are producing highly coloured, opaque photocatalytic samples, such as paints and tiles for example, for which a ready method for demonstrating their efficacy as photocatalytic materials does not at present exist.

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